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Description

The present invention relates to photosensitive compositions and materials employing them.

U.S. Patents 4,399,209 and 4,440,846 to The Mead Corporation describe imaging materials and imaging processes in which images are formed through exposure controlled release of an image-forming agent from a microcapsule containing a photohardenable composition. The imaging material is exposed image-wise to actinic radiation and subjected to a uniform rupturing force. Typically the image-forming agent is a colour precursor which is released image-wise from the microcapsules whereupon it reacts with a developer to form a visible image.

One of the problems which has been encountered in designing commercially acceptable panchromatic, full colour imaging materials employing these techniques has been the relatively short wavelengths band to which most photohardenable compositions are sensitive to actinic radiation. In most cases, the compositions are only sensitive to ultraviolet radiation or blue light, e.g., 350 to 480 nm.

Full colour photosensitive materials are described in our British Patent 2113860 and in our European Patent Application No. 85303484.1 (EP-A-0164931).

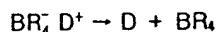
These imaging materials include a photosensitive layer which contains three sets of microcapsules. Each set of microcapsules is sensitive to a different band of radiation in the ultraviolet or blue spectrum and contains a cyan, magenta or yellow image-forming agent. The absorption spectra of the initiators employed in these microcapsules are never perfectly distinct. There is always some degree of overlap in the absorption curves and sometimes it is substantial. Exposure conditions therefore must be controlled carefully to avoid cross-exposure.

It would be desirable to extend the sensitivity of the photohardenable compositions used in these imaging materials to longer wavelengths. By extending the sensitivity of the photohardenable compositions to longer wavelengths, the amount of overlap in the absorption spectra of the initiators and the concomitant incidence of cross-exposure can be reduced. It would be particularly desirable if compositions could be designed with sensitivities to selected wavelength bands throughout the visible spectrum (400 to 700 nm) since this would provide a visible light-sensitive material which could be exposed by direct reflection or transmission imaging and without image processing.

We have found that photohardenable compositions may be prepared which comprise a free radical addition polymerizable or crosslinkable compound and an ionic dye-reactive counter ion compound, the ionic dye-reactive counter ion compound being capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization or crosslinking of the polymerizable or crosslinkable compound, the ionic dye being selected from the group consisting of methine, polymethine, triarylmethane, indoline, thiazine, xanthene, oxazine, acridine and oxonol dyes.

We have found that ionic dye-reactive counter ion compounds, such as cationic dye-borate anion compounds, are useful photoinitiators of free radical addition reactions. Such compounds consist of a visible light absorber (the ionic dye) ionically bonded to a reactive counter ion. The counter ion is reactive in the sense that upon excitation of the dye, the counter ion donates an electron to or accepts an electron from the excited dye. This electron transfer process generates radicals capable of initiating polymerization of a monomer.

The mechanism whereby the compounds absorb energy and generate free radicals is not entirely clear. It is believed that upon exposure to actinic radiation, the dye ion is excited to a singlet state in which it accepts an electron from or donates an electron to the counter ion. For a cationic dye-borate anion compound, this can be illustrated by the following equation:



The lifetime of the dye singlet state is extremely short by comparison to the lifetime of the triplet state. The quenching rate constants which have been observed suggest that the ionic compounds experience a very efficient electron transfer via the singlet state. In solution in the polymerizable compound, tight ionic pairing of the counter ion and the dye is believed to provide favourable spacial distribution promoting electron transfer to such an extent that the transfer occurs even though the lifetime of the singlet state is very short. Of course, this does not mean that electron transfer is restricted to the singlet state. Ionic dyes which have significant populations of triplet state may undergo electron transfer through the singlet state, triplet state, or both singlet and triplet states.

Upon transfer of the electron, a radical is formed. Many of the ionic compounds we have found useful as initiators in practice of the present invention do not appear to exhibit significant back electron transfer. It is believed that following electron transfer, the dye and counter ion become disassociated such that back

electron transfer does not occur.

The ionic compounds described in more detail below used in practice of the present invention differ from the collision generated species encountered in other photosensitive systems such as collision complexes which yield encounter complexes, exciplexes and/or contact ion pairs. See for example, 5 Kavarnos et al., "Photosensitization by Reversible Electron Transfer", Chem. Rev. 401(1986).

Where the ionic dye and the counter ion are present in the photopolymerizable composition as a stable, non-transient compound, and not as a dissociated ion pair, formation of the compound is not dependent upon diffusion and collision. As distinguished from photographic materials and compositions containing collision dependent complexes, in the present compositions essentially all of the sensitizing dye present in 10 the photosensitive materials prior to exposure is ionically bonded to the counter ion.

The ionic compounds we have found useful as initiators in practice of the present invention can also be characterised in that they are soluble in nonpolar solvents such as trimethylolpropane triacrylate (TMPTA) and the like. They are soluble in an amount of at least about 0.1%, and preferably, at least about 0.3% by weight. While these amounts are not large, they are substantial considering the normally lower solubility of 15 ionic materials in polar solvents. While the compounds are soluble, the dye and the counter ion do not dissociate in solution. They remain ionically bonded to each other.

In dye-sensitized photopolymerizable compositions, visible light is absorbed by a dye having a comparable absorption band, the dye is raised to its excited electronic state, the lifetime of which may be 10^{-9} to 10^{-3} second, depending upon the nature (singlet or triplet) of the excited state. During this time, the 20 absorbed energy allows an electron to be transferred to or from the dye molecule to produce the free radical. In prior initiator systems, this transfer is diffusion controlled. The excited dye must interact (collide) with another molecule in the composition which quenches the dye and generates a free radical. In the present invention, the efficiency with which the excited state is utilized is not limited by diffusion.

Thus, these systems provide a means for generating free radicals from the excited state of an ionic dye 25 and in so doing provide photohardenable compositions which are sensitive at longer wavelengths.

One of the particular advantages of using ionic dye-counter ion compounds as initiators of free radical addition reactions is the ability to select from a wide variety of dyes which absorb at substantially different wavelengths. The absorption characteristics of the compound are principally determined by the dye. Thus, by selecting a dye which absorbs at 400 nm or greater, the sensitivity of the photosensitive material can be 30 extended well into the visible range. Furthermore, compounds can be selected which are respectively sensitive to red, green and blue light without substantial cross-talk.

The invention provides, in a first aspect thereof, a dental composition which comprises a polymerizable composition comprising:

- a photopolymerizable acrylate based adhesive material; and
- 35 a photoinitiator;

wherein said photoinitiator comprises an ionic dye-counter ion compound capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization of said photopolymerizable acrylate based adhesive material;

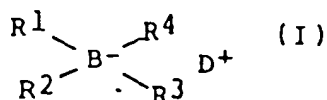
and an inert dental filler material.

40 According to an alternative aspect thereof, the invention provides a photopolymerizable composition comprising an acrylate based adhesive material, and a photoinitiator, wherein said photoinitiator comprises an ionic dye-counter ion compound capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization of said acrylate based adhesive material, for use in a dental treatment comprising applying said composition to a dental surface;

45 exposing the dental surface to actinic radiation to initiate photopolymerization; and curing said adhesive material.

Reference is made to the description of our U.S. Patents 4,399,209 and 4,440,846, our British Patent 2113860 and our European Patent Application 85303484.1 (EP-A-0164931).

Cationic dye-borate anion compounds are known per se in the art. Their Preparation is described in U. 50 S. Patents 3,567,453; 4,307,182; 4,343,891; 4,447,521; and 4,450,227. Suitable such compounds found used in the practice of the present invention can be represented by the general formula (I):



Representative examples of alkyl groups represented by R^1 - R^4 are methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, stearyl, etc. The alkyl groups may be substituted, for example, by one or more halogen, cyano, acyloxy, acyl, alkoxy, or hydroxy groups.

Representative examples of aryl groups represented by R^1 - R^4 include phenyl, naphthyl, and substituted aryl groups such as anisyl. Alkaryl groups include methylphenyl and dimethylphenyl. Representative examples of aralkyl groups represented by R^1 - R^4 groups include benzyl. Representative alicyclic groups include cyclobutyl, cyclopentyl, and cyclohexyl groups. Examples of an alkynyl group are propynyl and ethynyl, and examples of alkenyl groups include a vinyl group.

As a general rule, useful ionic dye compounds must be identified empirically; however, potentially useful dye and counter ion combinations can be identified by reference to the Weller equation (Rehm, et al., Isr. J. Chem. 8, 259 (1970), which can be simplified as follows.

$$\Delta G = E_{ox} - E_{red} - E_{h\nu} \quad (\text{Eq. 3})$$

where ΔG is the change in the Gibbs free energy, E_{ox} is the oxidation potential of the borate anion BR_4^- , E_{red} is the reduction potential of the cationic dye, and $E_{h\nu}$ is the energy of light used to excite the dye. Useful compounds will have a negative free energy change. Similarly, the difference between the reduction potential of the dye and the oxidation potential of the borate must be negative for the compounds to be dark stable, i.e., $E_{ox} - E_{red} > 0$.

As indicated, Eq. 2 is a simplification and it does not absolutely predict whether a compound will be useful in the present invention or not. A number of other factors will influence this determination. One such factor is the effect of the monomer on the compound. Another factor is the radial distance between the ions. It is also known that if the Weller equation produces too negative a value, deviations from the equation are possible. Furthermore, the Weller equation only predicts electron transfer, and does not predict whether a particular compound is an efficient initiator of polymerization. The equation is a useful first approximation.

Specific examples of cationic dye-borate anion compounds useful in the practice of the present invention are shown in the following table with their λ_{max} .

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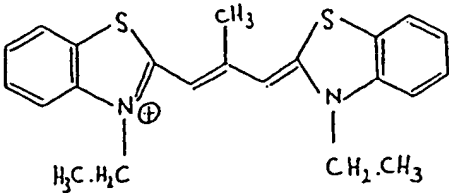
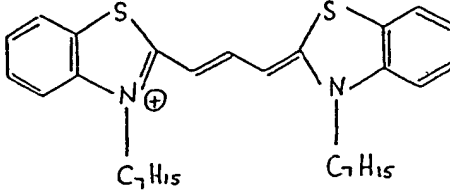
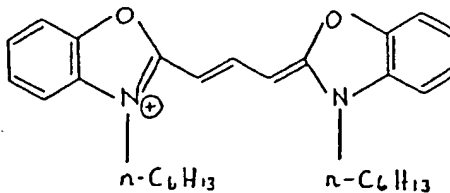
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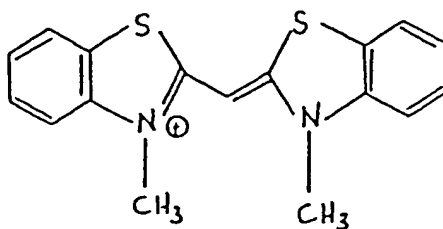
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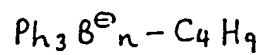
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<u>Compound No.</u>	<u>Table</u> <u>Structure</u>	<u>λ_{\max} (THPTA)</u>
5		
10		
1.	 <p data-bbox="776 659 954 709">$\text{Ph}_3\text{B}^{\ominus}\text{n-C}_4\text{H}_9$</p>	552 nm
15		
20		
2.	 <p data-bbox="776 1052 954 1102">$\text{Ph}_3\text{B}^{\ominus}\text{n-C}_4\text{H}_9$</p>	568 nm
25		
30		
35		
3.	 <p data-bbox="792 1482 971 1522">$\text{Ph}_3\text{B}^{\ominus}\text{n-C}_4\text{H}_9$</p>	492 nm
40		
45		
50		
55		

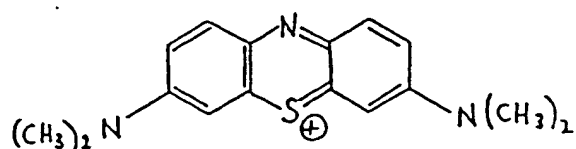
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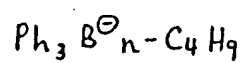
428 nm



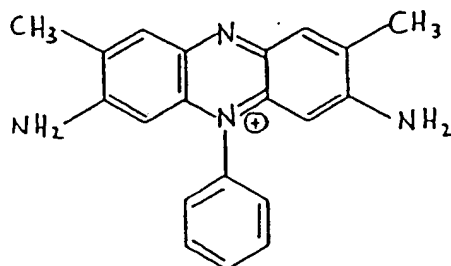
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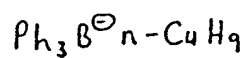
658 nm



6.

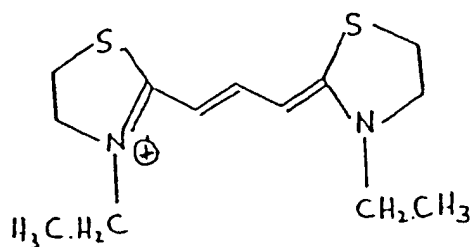


528 nm



7.

450nm

 $\text{Ar}_3 \text{B}^\ominus - \text{R}'$ No.R'Ar

7A

n-butyl

phenyl

7B

n-hexyl

phenyl

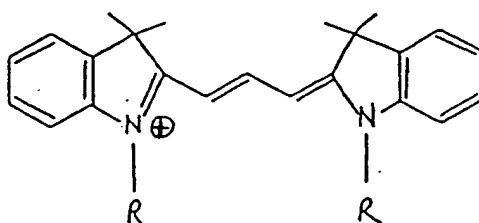
7C

n-butyl

anisyl

8.

550nm

 $\text{Ar}_3 \text{B}^\ominus - \text{R}'$ No.R'RAr

8A

methyl

n-butyl

phenyl

8B

methyl

n-hexyl

phenyl

8C

n-butyl

n-butyl

phenyl

8D

n-butyl

n-hexyl

phenyl

8E

n-heptyl

n-butyl

phenyl

8F

n-heptyl

n-hexyl

phenyl

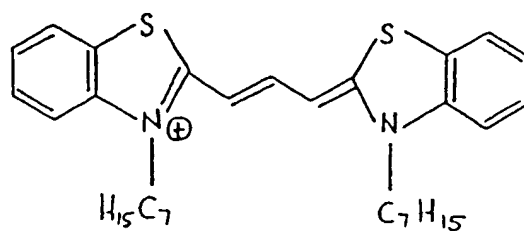
8G

ethyl

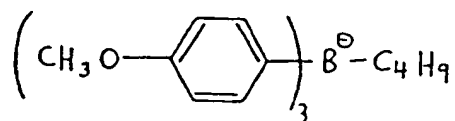
n-butyl

phenyl

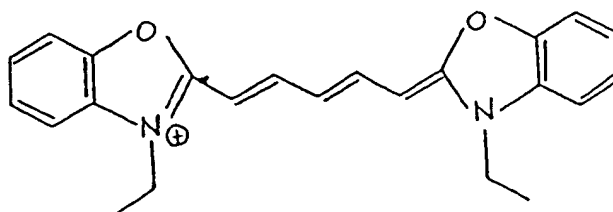
9.



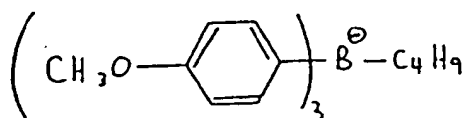
570 nm System



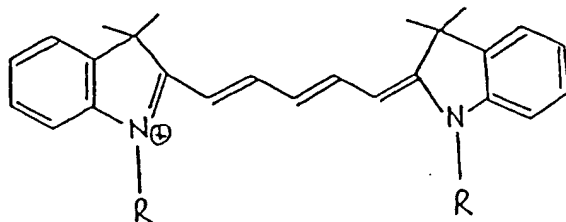
10.



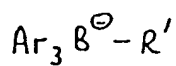
590 nm System



11.

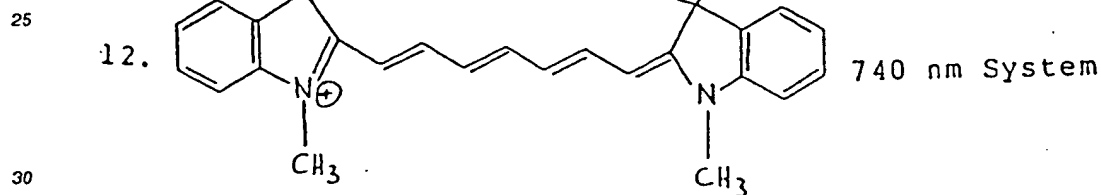


640 nm



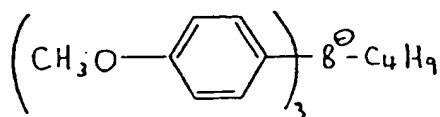
	<u>No.</u>	<u>R</u>	<u>R'</u>	<u>Ar</u>
5	11A	methyl	n-butyl	phenyl
	11B	methyl	n-hexyl	phenyl
	11C	n-butyl	n-butyl	phenyl
	11D	n-butyl	n-hexyl	phenyl
10	11E	n-pentyl	n-butyl	phenyl
	11F	n-pentyl	n-hexyl	phenyl
	11G	n-heptyl	n-butyl	phenyl
15	11H	n-heptyl	n-hexyl	phenyl
	11I	methyl	n-butyl	anisyl

20



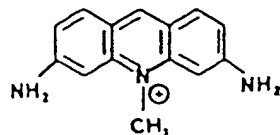
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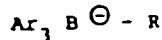
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13.



462 nm

45

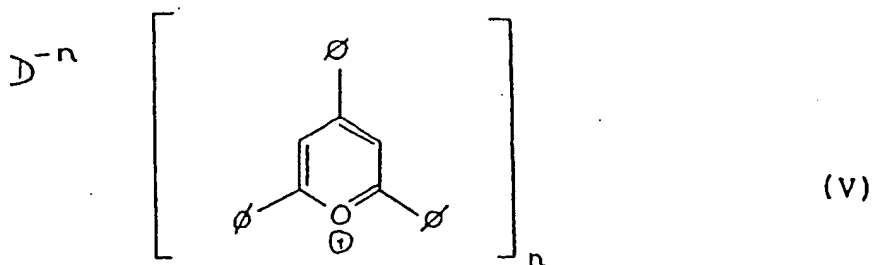


50 The cationic dye-borate anion compounds can be prepared by reacting a borate salt with a dye in a counter ion exchange in a known manner. See Hishiki, Y., Repts. Sci. Research Inst. (1953), 29, pp 72-79 Useful borate salts are sodium salts such as sodium tetraphenylborate, sodium triphenylbutylborate, sodium trianisylbutylborate and ammonium salts such as tetraethylammonium tetraphenylborate.

55 Anionic dye compounds are also useful in practise of of the present invention. Anionic dye-iodonium ion compounds of the formula (IV):



where D^- is an anionic dye and R^5 and R^6 are independently selected from aromatic nuclei such as phenyl or naphthyl and n is 1 or 2; and anionic dye-pyryllium compounds of the formula (V):

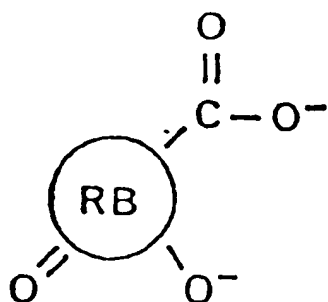


where D^- and n are as defined above are typical examples of anionic dye complexes.

Representative examples of anionic dyes include xanthene and oxonol dyes. For example Rose Bengal, eosin, erythrosin, and fluorescein dyes are useful. In addition to iodonium and pyryllium ions, other compounds of anionic dyes and sulfonium and phosphonium cations are potentially useful.

As in the case of the cationic dye compounds, useful dye-cation combinations can be identified through the Weller equation as having a negative free energy.

Selected examples of anionic dye compounds are shown in Table 2 (λ max. ca. 570 nm in TMPTA). In Table 2 the symbol ϕ is used for a phenyl group and the structure



is used for

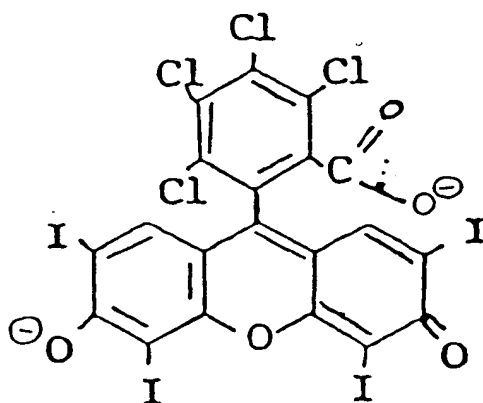
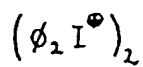
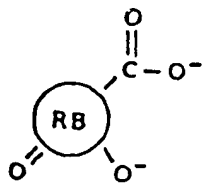


Table 2

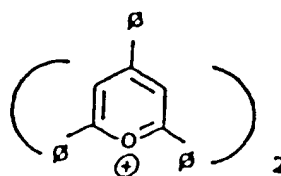
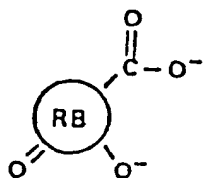
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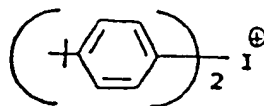
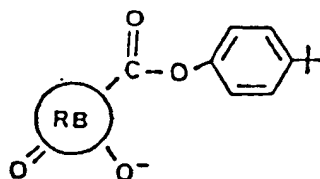
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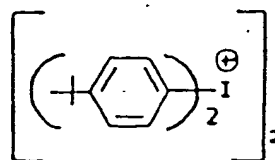
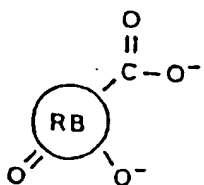
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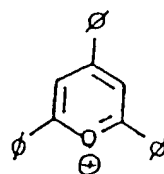
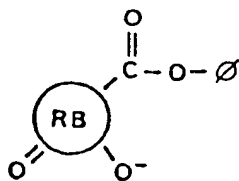
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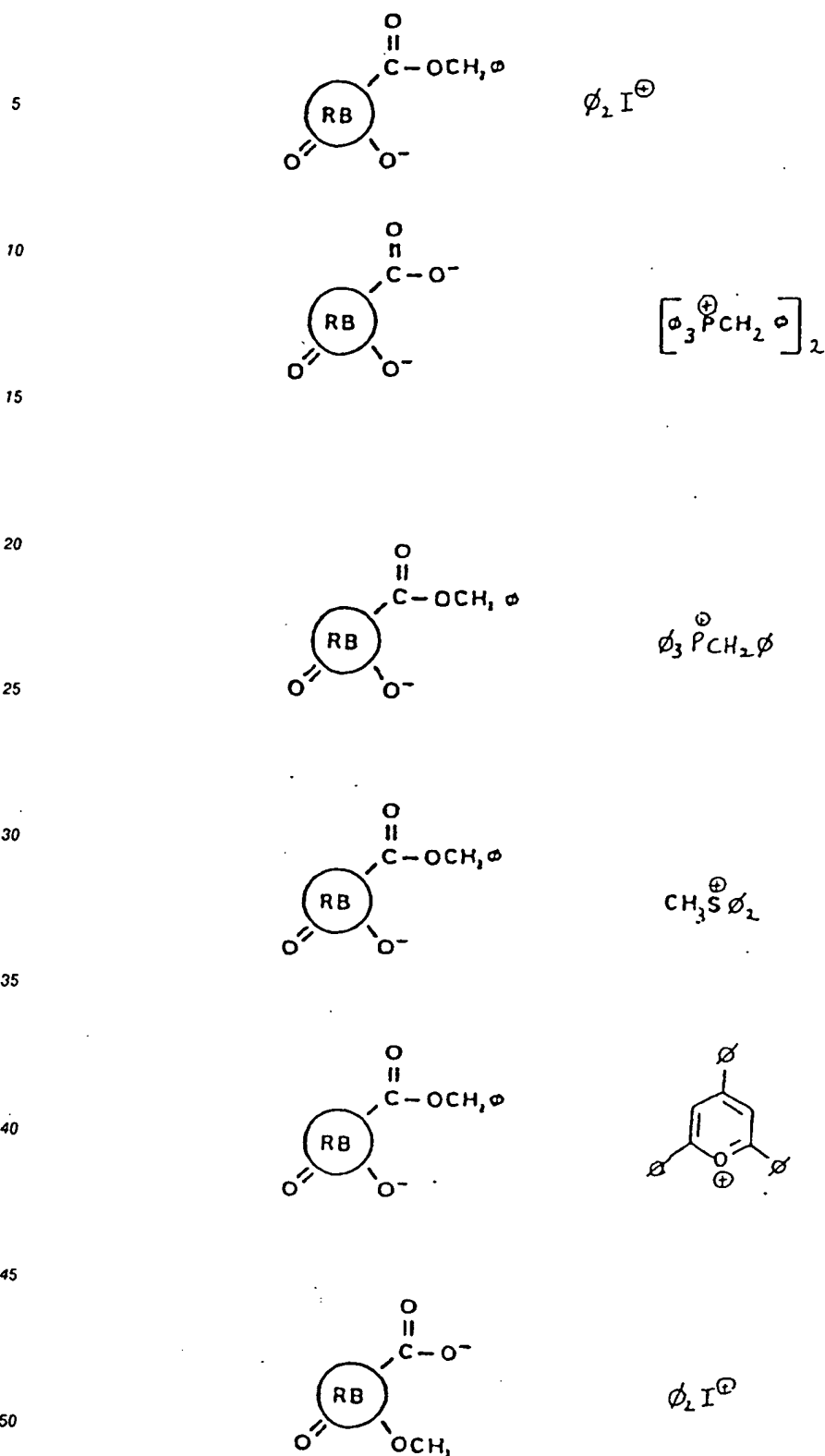


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The most typical examples of a free radical addition polymerizable or crosslinkable compound useful in practice of the present invention is an ethylenically unsaturated compound and, more specifically, a polyethylenically unsaturated compound. These compounds include both monomers having one or more ethylenically unsaturated groups, such as vinyl or allyl groups, and polymers having terminal or pendant ethylenic unsaturation. Such compounds are well known in the art and include acrylic and methacrylic

esters of polyhydric alcohols such as trimethylolpropane and pentaerythritol; and acrylate or methacrylate terminated epoxy resins, acrylate or methacrylate terminated polyesters. Representative examples include ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropane triacrylate (TMPTA), pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol hydroxypentacrylate (DPHPA),
 5 hexanediol-1,6-dimethacrylate, and diethyleneglycol dimethacrylate.

The ionic dye compound is usually used in an amount up to about 1% by weight based on the weight of the photopolymerizable or crosslinkable species in the photohardenable composition. More typically, the compound is used in an amount of about 0.2% to 0.5% by weight.

While the compound can be used alone as the initiator, film speeds tend to be quite slow and oxygen
 10 inhibition is observed. It has been found that it is preferable to use the compound in combination with an autoxidizer. An autoxidizer is a compound which is capable of consuming oxygen in a free radical chain process.

Examples of useful autoxidizers are N,N-dialkylanilines. Examples of preferred N,N-dialkylanilines are dialkylanilines substituted in one or more of the ortho-, meta-, or para- position by the following groups:
 15 methyl, ethyl, isopropyl, t-butyl, 3,4-tetramethylene, phenyl, trifluoromethyl, acetyl, ethoxycarbonyl, carboxy, carboxylate, trimethylsilylmethyl, trimethylsilyl, triethylsilyl, trimethylgermanyl, triethylgermanyl, trimethylstannyl, triethylstannyl, n-butoxy, n-pentyloxy, phenoxy, hydroxy, acetyl-oxy, methylthio, ethylthio, isopropylthio, thio-(mercapto-), acetylthio, fluoro, chloro, bromo and iodo.

Representative examples of N,N-dialkylanilines useful in our compositions are 4-cyano-N,N-
 20 dimethylaniline, 4-acetyl-N,N-dimethylaniline, 4-bromo-N,N-dimethylaniline, ethyl 4-(N,N-dimethylamino) benzoate, 3-chloro-N,N-dimethylaniline, 4-chloro-N,N-dimethylaniline, 3-ethoxy-N,N-dimethylaniline, 4-fluoro-N,N-dimethylaniline, 4-methyl-N,N-dimethylaniline, 4-ethoxy-N,N-dimethylaniline, N,N-dimethylthioaniline, 4-amino-N,N-dimethylaniline, 3-hydroxy-N,N-dimethylaniline, N,N,N',N'-tetramethyl-1,4-dianiline and 4-acetamido-N,N-dimethylaniline.

Preferred N,N-dialkylanilines are substituted with an alkyl group in the ortho-position and include 2,6-diisopropyl-N,N-dimethylaniline, 2,6-diethyl-N,N-dimethylaniline, N,N,2,4,6-pentamethylaniline (PMA) and p-
 25 t-butyl-N,N-dimethylaniline.

Another useful class of autoxidizer is thiols such as mercaptobenzoxazoles, mercaptotetrazines, and mercaptotriazines. Specific examples of useful thiols include: 2-mercaptobenzothiazole, 6-ethoxy-2-mercap-
 30 tobenzothiazole, 2-mercaptobenzoxazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 2-mercapto-1-methylimidazole, 2-mercapto-5-methylthio-1,3,4-thiadiazole, 5-n-butylthio-2-mercapto-1,3,4-thiadiazole, 4-methoxybenzenethiol, 1-phenyl-1H-tetrazole-5-thiol, 4-phenyl-4H-1,2,4-triazole-3-thiol, 2-mercaptobenzimidazole, pentaerythritol tetrakis(mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), trimethylolpropane tris(mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), 4-acetamidothiophenol, mercaptosuccinic
 35 acid, dodecanethiol, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercapto-3H-quinazoline, and 2-mercaptothiazoline.

The autoxidizers are preferably used in concentrations of about 4-5% by weight.

In some cases, the ionic dye compounds generate radicals upon heating, i.e., they behave as thermal
 40 initiators. This can cause the photosensitive composition to harden during storage at elevated temperatures which, in turn, detracts from the shelf life of the imaging system. To prevent thermal initiation and improve shelf life, it is desirable to include a thermal polymerization inhibitor in the internal phase. Where the dye is oxidized in the course of initiation, the thermal polymerization inhibitor is an antioxidant such as 2,6-di-t-butyl-4-methylphenol. Other useful thermal polymerization inhibitors are known per se and can also be used to improve shelf life.

45 Synthesis Examples 1 and 2 respectively illustrate the preparation of borates and dye-borate compounds.

SYNTHESIS EXAMPLE 1

50 Triphenylborane was dissolved in 150 ml dry benzene (1M) under nitrogen atmosphere. The flask was placed in a cool water bath and, while stirring, n-BuLi, (1.1 eq.) added via syringe. A white precipitate soon formed after addition was started. Stirring was continued about 45-60 min. 100 ml hexane was added and the precipitate was then filtered, washing with hexane. This resultant Li salt was slightly air unstable. The white powder was dissolved in about 200 ml distilled water and, with vigorous stirring, an aqueous solution
 55 of tetramethyl ammonium chloride (1.2 eq. of theoretical in 200 ml) was added. A thick white precipitate formed. this aqueous mixture was stirred for about 30 min. at room temperature, then filtered. The collected white solid was washed with distilled water.

As an alternative synthesis, to a 1.0M solution of 2.0 equivalents of 1-butene in dry, oxygen-free dichloromethane, under inert atmosphere, was added slowly dropwise with stirring, 1.0 equivalents of a 1.0M solution of dibromomethane-methylsulphide complex in dichloromethane. The reaction mixture was stirred at reflux for 36 hours and the dichloromethane and excess 1-butene were removed by simple distillation. Vacuum distillation of the residue afforded 0.95 equivalents of a colourless mobile oil (BP 66-7 0.35 mm Hg, $^1\text{H-NMR}$:bs (4.83PPM)). Under inert atmosphere, this oil was dissolved in dry, oxygen-free tetrahydrofuran to give a 1.0M solution and 3.0 equivalents of a 2.0M solution of phenylmagnesium chloride in tetrahydrofuran were added dropwise with stirring. After stirring 16 hours, the resultant solution was added slowly with vigorous stirring to 2 equivalents of tetramethylammonium chloride, as a 0.2 M solution, in water. The resulting white flocculate solid was filtered and dried to afford a near quantitative amount of the desired product Mp 250-2 °C, $^1\text{H-NMR}$:bs (-3.70PPM).

SYNTHESIS EXAMPLE 2

A suspension of a borate salt (1 g/10 ml) in MeOH was sonicated, to make a very fine suspension. The flask was protected from light by wrapping with aluminium foil then 1 equivalent of dye was added. This solution was stirred with low heat on a hot plate for about 30 min. It was allowed to cool to room temperature then diluted with 5-10 volumes of ice water. The resultant solid was filtered and washed with water until washings were colourless. It was suction filtered to dryness. The initiator compound was completely dried by low heat (about 50 °C) in a vacuum drying oven. Initiator is usually formed quantitatively. Analysis by H-NMR indicated 1:1 compound formation typically greater than 90%.

SYNTHESIS EXAMPLE 3

30 millimoles of neutral acriflavine was dissolved in 200 mls of hot CH_3OH . To this solution was added 30 millimoles of solid tetramethylammonium n-butyltriphenyl borate stirred in 100 mls of CH_3OH . To this resulting mixture was added 50 mls of acetone. The reaction solution was heated overnight and was filtered. The filtrate was treated with 500 mls of ice-water to produce 3.10 grams of acriflavine n-butyltriphenyl borate. This compound was dissolved in TMPTA at room temperature to give a yellow solution having a concentration of $7.05 \times 10^{-6} \text{ M}$. A drop of this solution was placed between two microscope slides and the slides were exposed to visible light. The microscope slides locked up demonstrating that the TMPTA had polymerized.

The present invention is illustrated in more detail by the following non-limiting Examples.

Embodiments of composition can be produced in accordance of the present invention which are adapted for use in connection with dental adhesives and compositions. Many commercially used adhesives are based upon photopolymerizable acrylate polymers. For example, commonly used adhesives are based upon bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane, sometimes referred to as diglycidyl methacrylate of bisphenol A. Representatives of such compounds are set forth in U.S. Patent Nos. 4,089,763; 4,459,193; 4,479,782; 4,490,115; 4,491,453; 4,515,930; 4,553,940; and at pages 501-508 and 515-517 of the Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7 (1979). These compounds require a photoinitiator and may also include an amount of an inert dental filler material. Examples of dental filler materials include natural materials such as quartz, feldstone, pottery stone, wallastonite, mica, clay, kaolin, and marble; ceramics such as silica, aluminum, silicon nitride, boron carbide, boron nitride, soda glass, barium glass, strontium glass, borosilicate glass, and lanthanum-containing glass ceramic; and water-insoluble inorganic salts such as barium sulfate and calcium carbonate. The preferred photoinitiators were usually based upon alpha diketones. These initiators are disadvantageous as they are low in efficiency and absorptivity. Further, it is necessary to use either ultraviolet or blue light to initiate photopolymerization.

We have found that instead of using an alpha diketone initiator our ionic dye-counter ion complexes may be used as photoinitiators. Preferred photoinitiators are the cationic dye-borate anion complexes. Use of these initiators enables light emitted from a broad band visible light source to photoadhere dental work to teeth. Thus, the requirement of using harmful ultraviolet rays is obviated. Alternately, commercially available inexpensive lasers may be used as the light source for the photopolymerization reaction.

The dental compositions may also optionally include pigments, opacifiers, brightening agents, handling agents and other modifcants.

The method of using these new dental adhesives and compositions follows, to an extent, the method currently practiced by those skilled in the art. The dental surface to be repaired is cleansed of decayed material and is acid etched to promote bonding. At this point, a bonding agent may be employed by coating

it upon the surface to be repaired. The present material, including inert dental filler, is then applied to the dental surface and molded to the surface according to conventional practices. The dental surface, including adhesive, is then exposed to visible light from a light source and the presence of the ionic dye-counter ion complex generates free radicals which initiate free radical polymerization or crosslinking of the acrylate based adhesive material and subsequently cures the adhesive material. When used in this manner, the composition functions both as an adhesive and as a dental restoration material.

Alternatively, our compositions may function solely as an adhesive. When used in this capacity, the dental surface is cleansed and the adhesive is thereafter applied to the surface. Dental restoration material is then applied onto the adhesive material and the dental surface is exposed to visible light to adhere the restoration material to the dental surface. When used in this configuration, the restoration material should be transparent to enable light waves to pass through said restoration material and contact the adhesive to initiate photopolymerization.

Obtaining a desired color for the adhesive can be controlled by the time length of exposure to actinic radiation. Prolonged exposure to the light source will bleach the photoinitiator, thereby preventing unusual discoloration. Alternatively, if the retention of color is desired for cosmetic purposes, a lesser exposure time should be utilized.

Claims

1. A dental composition which comprises a polymerizable composition comprising:
 - an photopolymerizable acrylate based adhesive material;
 - a photoinitiator;
 - wherein said photoinitiator comprises an ionic dye-counter ion compound capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization of said photopolymerizable acrylate based adhesive material;
 - and an inert dental filler material.
2. The composition according to claim 1 wherein said photoinitiator is a cationic dye-borate anion complex.
3. The composition according to any preceding claim wherein said photopolymerizable acrylate based adhesive material is based upon 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane.
4. The composition according to any preceding claim wherein said composition further comprises pigments, opacifiers, brightening agents or handling agents.
5. A photopolymerizable composition comprising an acrylate based adhesive material, and a photoinitiator, wherein said photoinitiator comprises an ionic dye-counter ion compound capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization of said acrylate based adhesive material, for use in a dental treatment comprising applying said composition to a dental surface; exposing the dental surface to actinic radiation to initiate photopolymerization; and curing said adhesive material.
6. A composition according to claim 5 for use in a dental treatment wherein said photoinitiator is a cationic dye-borate anion complex.
7. A composition according to claim 5 for use in a dental treatment wherein the actinic radiation is visible light.
8. A composition according to claim 7 for use in a dental composition wherein the visible light is provided from either a broad band visible light source or a laser.

Patentansprüche

1. Dentalverbindung mit einer polymerisierbaren Verbindung, umfassend:
 - einen Klebstoff, der auf einem fotopolymerisierbaren Acrylat basiert,

- einen Fotoinitiator, der eine ionische Farbstoff-Gegenion-Verbindung umfaßt, die dazu geeignet ist, aktinische (fotowirksame) Strahlung zu absorbieren und freie Radikale zu produzieren, die die radikalische Polymerisation des genannten, auf einem fotopolymerisierbaren Acrylat basierenden Klebstoffs einleiten,
 - 5 - und ein inertes Zahnfüllmaterial.
2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß der Fotoinitiator ein kationischer Farbstoff-Borat-Anionkomplex ist.
 - 10 3. Verbindung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der genannte, auf einem fotopolymerisierbaren Acrylat basierende Klebstoff auf 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-Propan basiert.
 4. Verbindung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Verbindung
 - 15 weiterhin Pigmente, Trübungsmittel, aufhellende Agentien oder Handhabungs-Agentien enthält.
 5. Fotopolymerisierbare Verbindung mit einem Klebstoff, der auf Acrylat basiert, und einem Fotoinitiator, der eine ionische Farbstoff-Gegenion-Verbindung umfaßt, die dazu geeignet ist, aktinische (fotowirksame) Strahlung zu absorbieren und freie Radikale zu produzieren, die die radikalische Polymerisation
 - 20 des genannten, auf einem fotopolymerisierbaren Acrylat basierenden Klebstoffs einleiten, zur Verwendung bei einer Zahnbehandlung, bei der die Verbindung auf eine Zahnoberfläche aufgebracht wird, die Zahnoberfläche einer aktinischen Strahlung ausgesetzt wird, um die Fotopolymerisation einzuleiten, und der Klebstoff zum Auszuhärten gebracht wird.
 - 25 6. Verbindung nach Anspruch 5 zur Verwendung in der Zahnbehandlung, dadurch gekennzeichnet, daß der Fotoinitiator ein kationischer Farbstoff-Borat-Anionkomplex ist.
 7. Verbindung nach Anspruch 5 zur Verwendung in der Zahnbehandlung, dadurch gekennzeichnet, daß die aktinische Strahlung sichtbares Licht ist.
 - 30 8. Verbindung nach Anspruch 7 zur Verwendung in einer Dentalverbindung, dadurch gekennzeichnet, daß das sichtbare Licht entweder von einer Breitband-Lichtquelle sichtbaren Lichts oder von einem Laser herrührt.

35 Revendications

1. Composition dentaire qui comprend une composition photopolymérisable comprenant:
 - un matériau adhésif à base d'acrylate photopolymérisable;
 - un photoinitiateur;
- 40 dans laquelle ledit photoinitiateur comprend un composé colorant ionique contre-ion capable d'absorber les radiations actiniques et de produire des radicaux libres qui initient une polymérisation radicalaire dudit matériau adhésif à base d'acrylate photopolymérisable; et
 - un matériau de remplissage dentaire inerte.
- 45 2. Composition selon la revendication 1 dans laquelle ledit photoinitiateur est un complexe colorant cationique-anion borate.
3. Composition selon l'une quelconque des revendications précédentes dans laquelle ledit matériau adhésif à base d'acrylate photopolymérisable est basé sur le 2,2-bis[4-(2-hydroxy-3-méthacryloxypropoxy)phényle]-propane.
- 50 4. Composition selon l'une quelconque des revendications précédentes dans laquelle ladite composition comprend en plus des pigments, des opacifiants, des agents de brillance ou des agents de maintien.
- 55 5. Composition photopolymérisable qui comprend un matériau adhésif à base d'acrylate, et un photoinitiateur, dans laquelle ledit photoinitiateur comprend un composé colorant ionique contre-ion capable d'absorber les radiations actiniques et de produire des radicaux libres qui initient une polymérisation radicalaire dudit matériau adhésif à base d'acrylate, pour utilisation dans un traitement dentaire

comprenant l'application de ladite composition sur la surface dentaire;
l'exposition de la surface dentaire aux radiations actiniques pour initier la photopolymérisation; et
la polymérisation dudit matériau adhésif.

- 5 6. Composition selon la revendication 5 pour utilisation dans un traitement dentaire dans laquelle ledit photoinitiateur est un complexe colorant cationique-anion borate.
7. Composition selon la revendication 5 pour utilisation dans un traitement dentaire dans laquelle les radiations actiniques proviennent de la lumière visible.
- 10 8. Composition selon la revendication 7 pour utilisation dans une composition dentaire dans laquelle la lumière visible est fournie par une source de lumière visible à large spectre ou par un laser.

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